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Nitrate Sensitization of Liquid Fuels
(Final Report)

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Nitrate Sensitization of Liquid Fuels

Final Report for PWGSC RFP W7702-8-R692

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SUMMARY

The aim of this contract was to study the effect of a nitrate-based sensitizer (IPN) on the combustion properties of fuel-air mixtures. The results from this study complement flame speed and flammability data from previous tests with sensitizers such as IPN and TEA. Data in the present study were obtained in two different facilities: an 8-cm heated shock tube and a 30-cm heated detonation tube. Ignition delay data was obtained in the 8-cm shock tube, using a pressure transducer mounted in the end-wall of the shock tube. Incident shock speeds were obtained from pressure traces. In the 30-cm tube, detonation wave velocities were obtained using ionization gages and pressure transducers, along with cell width data obtained from soot foils. In both facilities, stoichiometric hexane-IPN-air mixtures were used, including 100% IPN and air, and 100% hexane and air.

This report consists of:

Appendix 1: Paper entitled "Effects of Nitrates on Hydrocarbon-Air Flames and Detonations" by Zhang, Akbar, Thibault and Murray presented at the 17th International Colloquium on the Dynamics of Explosions and Reaction Systems, July 25-30, Heidelberg, Germany, 1999. The work presented in this paper was based on the results of this contract and experimental work in a previous contract.

Appendix 2: Ignition delay and end-wall pressure traces from tests in the 8-cm shock tube.

Appendix 3: Pressure, ionization traces and photographs of soot foils from tests in the 30-cm detonation tube.

Appendix 1

Paper Based on Results

Effects of nitrates on hydrocarbon-air flames and detonations

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Abstract

The subject of hydrocarbon sensitization by nitrates under conditions of a heterogeneous spray has been of interest due to its applicability in promoting ignition. The sensitizing effect has often been attributed to the promotion of hydrocarbon reaction kinetics via the formation of radicals. In fact, some nitrates can be considered to be fairly sensitive oxygenated fuels, or so-called "low-sensitivity condensed explosives". Hence, both the kinetics and energetics of nitrates may play a role in the sensitization of hydrocarbon combustion. To gain insight into the mechanisms of the nitrate sensitization effect, the present work was limited to vapour phase studies at elevated temperatures in order to avoid the influence of heterogeneous factors. The experiments performed included studies of flammability, flame propagation, shock ignition and detonation. The mixtures used were composed of air, isopropyl nitrate (IPN) and hydrocarbons, including methane, propane and hexane, with IPN concentrations ranging from 0 to 100 mole % in hydrocarbon-IPN. For the shock ignition and detonation experiments, the measured ignition delay and detonation cell size had minimum values for IPN-air and maximum values for hexane-air. With increases in the IPN concentration, the ignition delay and detonation cell size fell monotonically between the values for hexane and IPN. This monotonic behaviour was explained to be the result of the lower activation energy and comparable energetics of IPN versus hexane, which promoted the reaction rate and therefore reduced the ignition delay and the detonation cell size of the mixtures. For the slow combustion mode, the results also confirmed the monotonic behavior and showed that the lean flammability limit and the flame velocity fell between that of the hydrocarbon and IPN.

Key words: Explosion, Detonation, Heterogeneous explosion, Shock ignition delay, Flame, Nitrates, Hexane

1 Introduction

Shock ignition and detonation of a spray that consists of liquid fuel droplets and a gaseous oxidizer have been investigated since the 1960's. A comprehensive review of the earlier studies can be found in the paper by Sichel (1982). It is known that the detonation of a spray is predominantly controlled by three time scales: the droplet breakup time, the vapourization time and the chemical reaction time of the vapour. For a spray with large fuel droplets (~ 10^2 – 10^3 μm) and low vapour pressure, such as decane and kerosene, the "quasi-detonation" process is dominated by the droplet breakup mechanism (Dabora et al. 1968, 1969, 1972; Borisov et al. 1970; Lu and Slagg 1972; Bar-Or et al. 1981). The general sequence of the break-up mechanism is: 1) formation of a fuel micro-mist in the droplet wake by the breakup of fuel droplets via boundary layer stripping and Taylor instability; 2) ignition and explosion of the micro-mist that generate a blast wave, which ignites the rest of the droplet and supports the propagation of the leading shock front. When the droplet size is decreased (~ 10^1 – 10^0 μm) and the vapour pressure is elevated by increasing the temperature or using a high vapour pressure fuel, such as hexane, heptane or propylene oxide, the spray detonation mechanism is shifted to vapour-phase detonation which is characterized by its transverse wave structure (Bar-Or et al. 1981; Bull 1981; Benedick et al. 1991; Murray and Gerrard 1990).

The sensitization of hydrocarbon liquid fuels by additives such as nitrates has been of interest in promoting the ignition of a spray detonation wave in air with large fuel droplets or low vapour pressures (Lu and Slagg 1972, 1974, 1977; Lin et al. 1984; Dabora 1980; Borisov et al. 1983a, 1983b). The literature on the detonability of some hydrocarbon fuels sensitized by propyl nitrate, $CH_3(CH_2)_2NO_3$, is summarized in Table 1. This clearly shows that the addition of propyl nitrate (NPN) broadens both the lean and rich detonation limits. The type of nitrates used also significantly reduces the ignition delay and initiation energy. Zaslonko et al. (1985, 1988) attribute the sensitizing effect of nitrates to the promotion of reaction kinetic via the formation of RO and NO_2 radicals and their further bifurcation into smaller radicals and atoms. In fact, some nitrates, which contain oxygen in their molecular structure, can be considered a monopropellant, which is generally known as a low-sensitivity condensed explosive with relatively high vapour pressure. Consequently, the reduction of the ignition delay caused by mixing a nitrate with hydrocarbons might be interpreted alternatively, i.e., micro-scale decomposition or explosion of nitrate particles which produce the heat and radicals. It is unclear whether the reduction of the ignition delay is caused by the radical kinetics alone or whether micro-scale explosion of nitrate particles plays a role. Recently, Tieszen et al. (1991) performed extensive detonation experiments of vaporized liquid fuels in air in a heated detonation tube 0.43 m in

diameter. Presles et al. (1996) also recently conducted detonation experiments in vaporized nitromethane. Experiments performed at 1 atm and 100 °C by Tieszen et al. revealed that detonation cell sizes for stoichiometric mixtures of hexane, octane, decane and JP-4 ranged between 40 and 60 mm, whereas the detonation cell size for hexyl nitrate-air was 11 mm, 5 times smaller than that of hexane-air. Although no experiments were reported for vaporized hydrocarbon fuel mixed with nitrates, these experiments, supported by detailed kinetic calculations, provide a significant step in understanding the sensitization effect of nitrates.

Table 1. Detonation limits of sprays in air in tubes

Fuel	Droplet size, μm	B. P., °C @ 1atm	Lean limit ϕ	Rich limit ϕ	Initiation	Ref.
Hexane* (C_6H_{14})	6-17	69	0.8	1.7	tetryl, 25-110 g	1
Heptane (C_7H_{16})	~10	99	0.65	1.6	He driver	2
Heptane + 20% NPN	~10	---	0.6	3.6	He driver	2
Heptane	~700	99	no deton.	no deton.	He driver	2
Heptane + 20% NPN	~700	---	0.28	2.26	He driver	2
Kerosene ($C_{11.6}H_{23.2}$)	~780	175-200	no deton.	no deton.	He driver, M_0=3.2	3
Kerosene + 10 % NPN	~780	---	0.3-0.44	---	He driver, M_0=3.2	3
Kerosene + 20 % NPN or butyl nitrite	~780	---	< 0.3	---	He driver, M_0=3.2	3
Decane* ($C_{10}H_{22}$)	9 - 30	174	no deton.	no deton.	tetryl, 25 g	1
Decane**	~20 - 50	174	no deton.	no deton.	quasi-planar detonation initiator	4
Decane	~400	174	no deton	no deton.	$2H_2/O_2$/He initiator, 0.68 – 1 atm	5
Decane + 12 % NPN	~400	---	< 0.98	---	$2H_2/O_2$/He initiator, 0.68 – 1 atm	5
Decane + 25 % NPN	~400	---	< 0.9	> 2.83	$2H_2/O_2$/He initiator, 0.68 – 1 atm	5
Decane, 20 °C	~400	174	---	2.49	$2H_2/O_2$/He initiator, 2.7 atm	6
Decane, 40 – 50 °C	~400	174	---	≥ 3.29	$2H_2/O_2$/He initiator, 2.7 atm	5

* 125 μm Polyethylene-confined cylindrical 5 m^3 cloud with a diameter of 2.2 m; spherical tetryl charge initiation.
** Unconfined 80 m^3 cloud with a cross section of 7 x 2-4 m^2; 850 g and 0.3 x 1.2 m^2 detasheet initiation or 1.5 m long propylene oxide – air cloud detonation initiator.
Ref. 1. Bull et al. 1981; 2. Lu et al. 1977; 3. Dabora 1980; 4. Benedick et al. 1991; 5. Lin et al. 1984; 6. Tang et al. 1986.

The vapour phase studies exclude the influences associated with the multiphase transport time scales, and therefore provide a lower limit approach to further investigate the sensitizing mechanisms of nitrates. Thus, the present experimental work will focus on vapour phase mixtures composed of nitrates and hydrocarbon fuels mixed with air. Unlike most of the previous work, where nitrate

additives ranged between 10 and 25 % in the total amount of fuel and additive, this work extends the nitrate additive range between 0 and 100 mole % in the total amount of fuel and additive. Hence, it can be determined whether the nitrates have a strong sensitizing effect at low concentrations or whether the nitrate concentration monotonically elevates the sensitivity of a hydrocarbon fuel, as when different-sensitivity fuels are mixed. The sensitizing effect will also be examined in flames and detonations to determine the dependence of sensitization on the combustion mode. Experiments for flammability limits, flame velocities, ignition delays behind reflected shocks, and detonation cell sizes are included.

2 Experiments

Methane, propane and hexane were used as hydrocarbon fuels. Isopropyl nitrate (IPN) was chosen as the nitrate additive, ranging from 0 to 100 mole % in the total amount of hydrocarbon and IPN. The standard heat of formation of the hydrocarbons and IPN, as well as their boiling point at 1 atm, are summarized in Table 2 (NPN is listed for comparison). Experiments for flammability limits, flame velocities, ignition delays and detonations were conducted in vapour phase fuel-additive-air mixtures at elevated temperatures above the boiling point of IPN.

Table 2. Properties of fuels and additives

Material	Formula	Heat of formation kJ/mole	Boiling Point °C @ 1 atm
Methane	CH_4	-74.6 (G)	-164
Propane	C_3H_8	-120.9 (L), -103.8 (G)	-42
Hexane	C_6H_{14}	-198.7 (L), -166.9 (G)	69
Isopropyl nitrate (IPN)	$(CH_3)_2CHNO_3$	-229.7 (L), -191.0 (G)	102
Propyl nitrate (NPN)	$CH_3(CH_2)_2NO_3$	-214.5 (L), -173.9 (G)	110

2.1 Flammability and flame velocity

Experiments for lean flammability limits and flame velocities were performed in a stainless steel tube, 5 cm in inner diameter and 1.58 m in length. The tube was vertical and closed at both ends. Mixtures were ignited at the bottom of the tube, and the flame propagation direction was upward. Prior to a test, the tube was heated to 115 ± 5 °C. Using the partial pressure rule at an initial pressure of 1 atm, fuel and dry air were introduced into the tube near its bottom, and the liquid sensitizing

additive was injected into the tube at its middle by a 0.5 ml injection needle. The mixture was then recirculated for 20 minutes to ensure a uniform mixture while the tube remained heated. The mixture was ignited with a spark generated by an 8 J Reynolds ignition system. The spark electrodes were made of copper and brass with a gap of 0.9 mm. To determine the flammability limit, a thermocouple was inserted into the centre of the tube at a position 0.95 m from the ignition spark. To obtain arrival times for determining the flame velocity, two ion gauges were also inserted into the tube centre. These were located at 0.64 m and 1.25 m from the ignition spark. Experiments were carried out for methane, propane and hexane sensitized by IPN.

2.2 Ignition delay

Ignition delay tests were conducted using a shock tube 8 cm in inner diameter. The driver section was 2 m in length and filled with helium or nitrogen to deliver different incident shock strengths. The driven section was 7.7 m long, with a Kulite pressure transducer located at the end wall to measure the ignition delay behind the reflected shock. The incident shock velocity was measured using Kulite pressure transducers located at 1 m from the end wall and on the end wall. Multiple sheets of mylar were used as diaphragms between the driver and the driven section. Prior to a test, the driven section was heated to 101 ± 8 °C as measured at 1 m, 5 m and 7 m from the diaphragm. The driver section was filled with helium between 9 and 11 atm for hexane-air vapour and with nitrogen from 5 to 12 atm for hexane-IPN-air vapour mixtures. Dry air was introduced into the driven section near the diaphragm and the liquid hexane and IPN were injected into the middle of the driven section. Test gas composition was determined by partial pressure measurements to the desired initial pressure of 0.25 atm. The mixture was then recirculated for 20 minutes to ensure a uniform mixture and temperature stabilization, while the tube remained heated. The diaphragms were ruptured using a piercing mechanism that consisted of a blade driven by an external air-actuated cylinder. An incident shock wave propagated in the test vapour and reflected from the driven section end wall where the ignition delay was measured.

2.3 Detonation

Experiments for the detonation of fuel-additive-air mixtures were performed in the heated detonation tube shown in Figs. 1 and 2. The facility has an inner diameter of about 0.3 m, and consists of a 4 m initiator, a 24 m test section and an 8 m relief section. The relief section was designed for a static pressure of 260 atm at 38 °C.. The relief section, connected to the test section and separated by a

diaphragm, is to reduce the possibility of the undesired pre-compression and the subsequent deflagration-detonation transition in the Craven and Greig scenario, which can cause very high pressures (Zhang et al. 1998). The initiator section was designed for a static pressure of 260 atm at 38 °C and can be filled with stoichiometric hydrogen-oxygen mixtures at various initial pressures. Five spark-plugs, one in the centre and four in a 0.142 m diameter circle, were mounted at the end plate of the initiator and connected to an 8 J Reynolds ignition system. This spark ignition system initiated a quasi-planar hydrogen-oxygen detonation wave which bursted a 3 mm nylon diaphragm between the initiator and test section and detonated the vapour mixture in the test section. The test section was designed for a static pressure of 130 atm at 38 °C. Electric band heaters were strapped to the outside surface and distributed uniformly along the entire length of the test section. These enable the facility to be heated up to 120 °C. Gauge ports were located at one meter intervals along the test section, with opposing ports in the last 6 m. Kulite pressure transducers and ion gauges were used to measure pressure, flame intensity and time of arrival. To record the detonation cell size, a 1 to 2 mm thick aluminum smoke foil, 0.5 m long and 0.94 m wide, was mounted cylindrically on the inner surface of the test section at a location just before the nylon diaphragm separating the test and relief sections. The final temperature of the vapour test mixture was automatically controlled to within ± 2 °C using two thermocouples and temperature controllers. The thermocouples were positioned to read the temperature of the test mixture, near the test-section centerline, at two locations along the length of the test section. The temperature of the detonation tube surface was periodically monitored during the heating process along the entire length of the test section. Dry air was introduced into the test section near the diaphragm. Two 0.5 litre stainless steel vessels containing pre-measured liquid hexane and liquid IPN were connected to the test section through a series of components including preset needle valves, isolating solenoid valves and gradually heated tubing. The desired test gas composition was achieved using the method of partial pressures. The gas was then recirculated for a period of time to ensure uniform mixing. The recirculation system temperature was automatically controlled to within 5 °C of the test section temperature.

The test procedure began by first evacuating the test section and filling it with dry air to about 0.5 atm. It was subsequently heated to 115 ± 2 °C over a period of 4 to 5 hours. When the target temperature was reached, the liquid fuel and nitrate were separately introduced into the test section using the preset needle valves and isolating solenoid valves. After the complete vaporization of the liquids, the test section was filled to an initial pressure of 1 atm with dry air. The mixture was then recirculated for 30 minutes while the facility remained heated. After recirculation of the test vapour mixture, the initiator was filled with stoichiometric hydrogen-oxygen to 2 atm in less than 5 minutes.

Finally, the detonation of the test vapour was initiated by the hydrogen-oxygen detonation wave originating in the initiator.

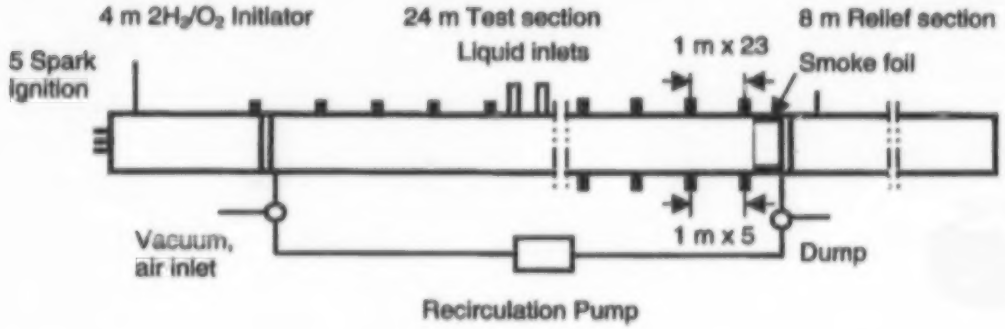


Figure 1. Schematic of the heated detonation tube.

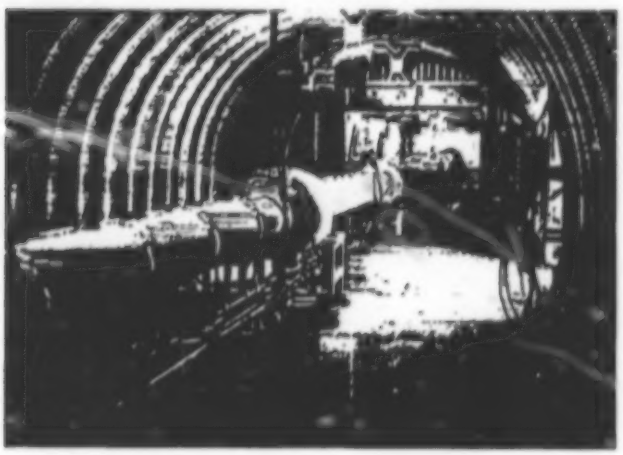


Figure 2. Heated detonation tube.

3 Results and discussion

3.1 Flammability and flame velocity

The flammability limits and flame velocity are rate-dependent and therefore reflect the mixture sensitivity in the slow combustion mode. The lean limits measured for methane, propane and hexane are in good agreement with the literature (Wagner et al. 1972). The results of the lean flammability limit tests for methane, propane and hexane in air, with increases in the IPN concentration, are

summarized in Fig. 3. The lean limit is expressed in terms of the equivalence ratio. The experiment for the lean limit was repeated three times for each point and the limit is accurate to within ± 0.1 mole %. The results indicate that with increases in the IPN concentration, the lean flammability limit of a fuel falls monotonically between that for the fuel and its additive.

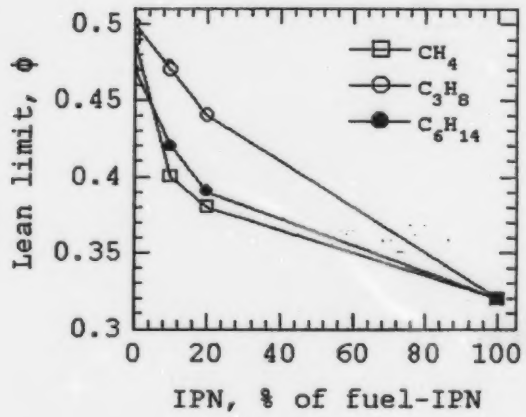


Figure 3. Lean flammability limit of fuel-IPN in air.

Figures 4 and 5 provide the flame velocity results for stoichiometric propane-IPN-air mixtures and hexane-IPN-air mixtures, respectively. The results show that the flame velocity varies monotonically between that for the fuel and its additive as the IPN concentration increases.

In summary, using IPN as an additive, the sensitivity of fuel-IPN-air mixtures in the slow combustion mode varies monotonically between that of the fuel and its additive. In addition, there is no obvious strong sensitizing effect at low concentrations of IPN.

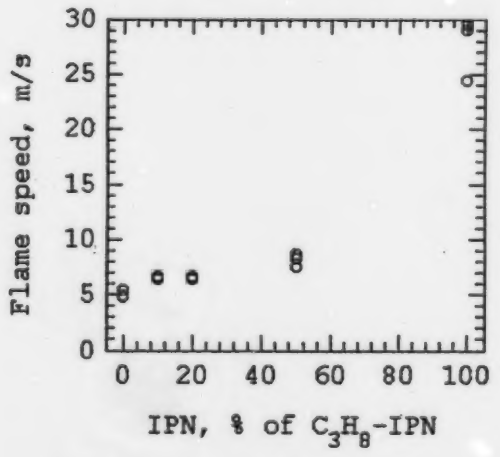


Figure 4. Flame velocity for stoichiometric C_3H_8-IPN-air mixtures.

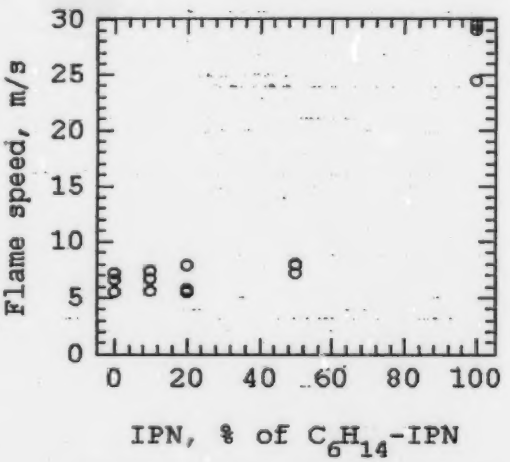


Figure 5. Flame velocity for stoichiometric C_6H_{14}-IPN-air mixtures.

3.2 Ignition delay

For the ignition delay tests, the incident shock velocity in the experiments ranged from 560 m/s to 1000 m/s. Figures 6 to 8 show some typical pressure histories at the end wall, for stoichiometric hexane-air, stoichiometric equimolar hexane-IPN in air, and stoichiometric IPN-air, respectively. The ignition delay was measured from the beginning of the reflected shock rise to the first explosion peak, as the slow rise at the "foot" of the explosion was easily seen in some cases, but in others it was often obscured by in the transducer ringing. Thus, the use of the first peak seemed to be the only consistent method applicable to all mixtures. The measured ignition delay is summarized in Fig. 9 for stoichiometric hexane-IPN-air mixtures where the IPN concentration varies from 0 to 100 mole % in hexane-IPN. The shock temperature in Fig. 9 was computed using shock Hugoniot calculations in the SuperSTATE code for a shock in frozen air (CDL 1996). The results in Fig. 9 clearly show that the shock ignition delay varies monotonically between that for the hydrocarbon fuel and IPN as the IPN concentration increases.

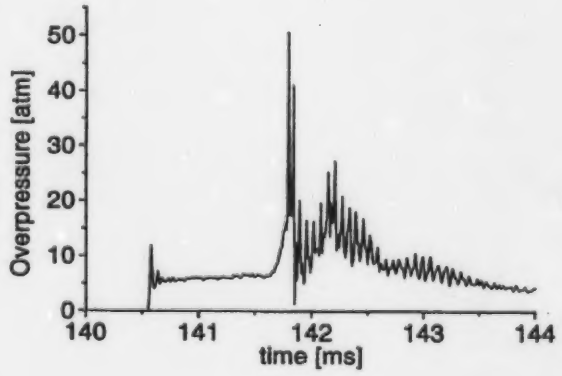


Figure 6. Pressure history on the end wall for an ignition delay test of stoichiometric hexane-air with an incident shock velocity of 921 m/s and a reflected shock temperature of 1136 K.

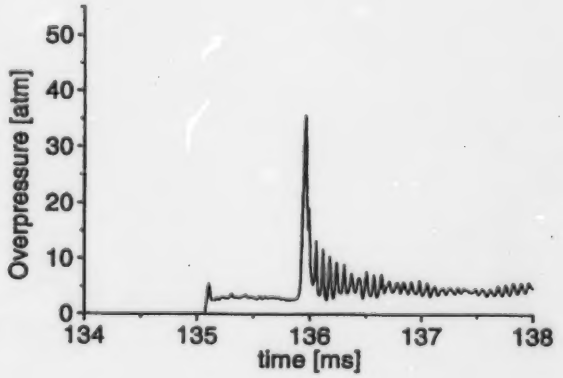


Figure 7. Pressure history on the end wall for an ignition delay test of stoichiometric (50% hexane + 50% IPN)-air with an incident shock velocity of 824 m/s and a reflected shock temperature of 975 K.

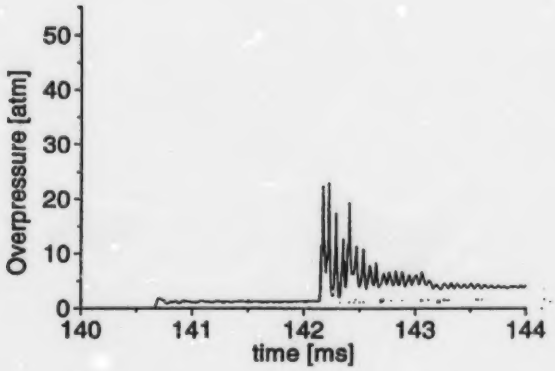


Figure 8. Pressure history on the end wall for an ignition delay test of stoichiometric IPN-air with an incident shock velocity of 563 m/s and a refelcted shock temperature of 595 K.

A least-squares fit to the ignition delay data was performed based on the Arrhenius global reaction law:

$$\tau = ke^{E/RT} \tag{1}$$

The fitted results are presented as solid lines in Fig. 9 and the values of the pre-exponential coefficient, k, and the effective activation energy, E, are given in Table 3. The results indicate that the effective activation energy is decreased as the IPN concentration increases in fuel-IPN mixtures.

Table 3. Kinetic coefficients of the global Arrhenius law

Mixture	E, kJ/mole	k, μs
Stoich. Hexane-air	61.47	1.707
Stoich. (50% hexane + 50% IPN)-air	41.59	1.946
Stoich. IPN-air	33.69	1.606

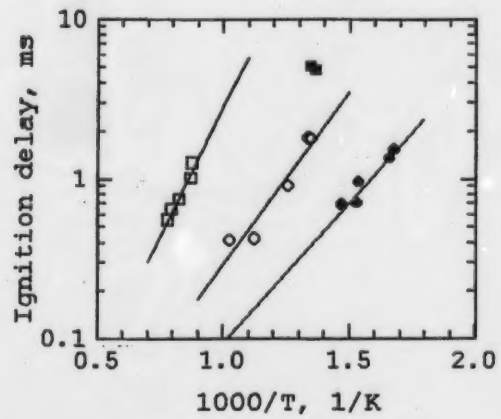


Figure 9. Ignition delay after the reflected shock for stoichiometric hexane-IPN-air mixtures. ●: IPN-air; O: (50% hexane + 50% IPN)-air; ■: (80% hexane + 20% IPN)-air; □: hexane-air.

3.3 Detonation

The stoichiometric hexane-IPN-air mixtures used for detonation experiments are listed in Table 4. Figures 10 through 12 show some typical pressure profiles of the detonation front for stoichiometric hexane-air, stoichiometric equimolar hexane-IPN in air, and stoichiometric IPN-air, respectively. The pressure traces were obtained in the test section, 21 m from the diaphragm separating the initiator and test sections. The apparently lower detonation front pressure for the stoichiometric equimolar hexane-IPN in air is probably due to the transverse wave influence. With increases in the IPN concentration, the increase in the oscillation frequency in the pressure profiles is indicative of the increased transverse wave frequency in the detonation front.

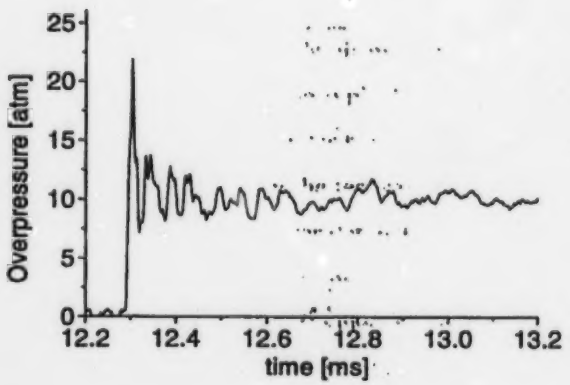


Figure 10. Detonation front pressure for stoichiometric hexane-air at 1 atm and 388 K.

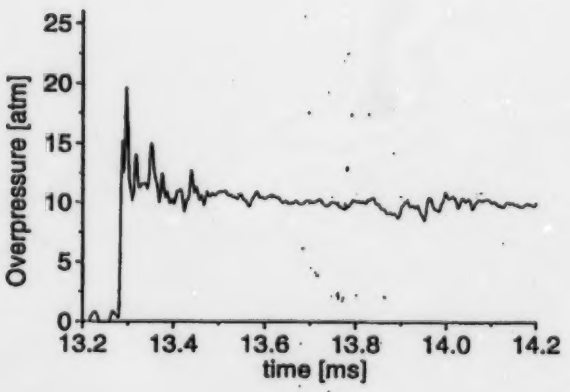


Figure 11. Detonation front pressure for stoichiometric (50% hexane + 50% IPN)-air at 1 atm and 388 K.

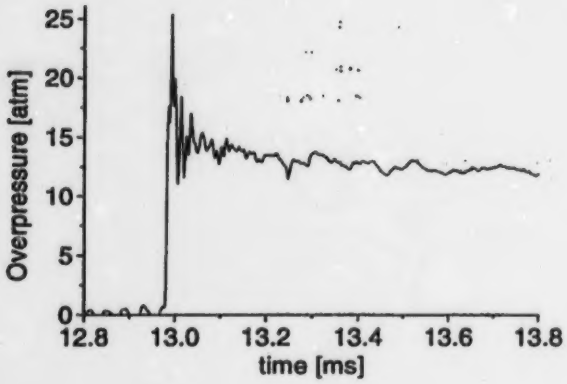


Figure 12. Detonation front pressure for stoichiometric IPN-air at 1 atm and 388 K.

The measured detonation velocities are shown in Table 4 and Fig. 13 and exhibit a spread of ± 1.5 %. The experimental detonation velocities are in agreement with those obtained from equilibrium thermodynamic calculations of CJ detonation using the SuperSTATE code (CDL 1996). In the calculations, the detonation products were assumed to be O_2, N_2, C, O, OH, H_2, H, H_2O, H_2O_2, N, NO, NO_2, NO_3, CO, CO_2 and HNO_3. The detonation velocity increases with IPN concentration since the energy release of IPN is higher than that of hexane.

Table 4. Vapour phase detonation data for stoichiometric hexane-IPN-air mixtures at 1 atm and 388 K.

Mixture	Mean cell width*, Mm	Standard deviation of cell width, mm	Deton. velocity, m/s	CJ deton. velocity, m/s
hexane-air	40	8.0	1792	1791
(90% hexane + 10% IPN)-air	32	5.2	1782	1795
(80% hexane + 20% IPN)-air	33	9.7	1800	1798
(50% hexane + 50% IPN)-air	23	5.3	1807	1814
IPN-air	8	1.5	1832	1865

* The cell width was measured as the distance between the two vertexes.

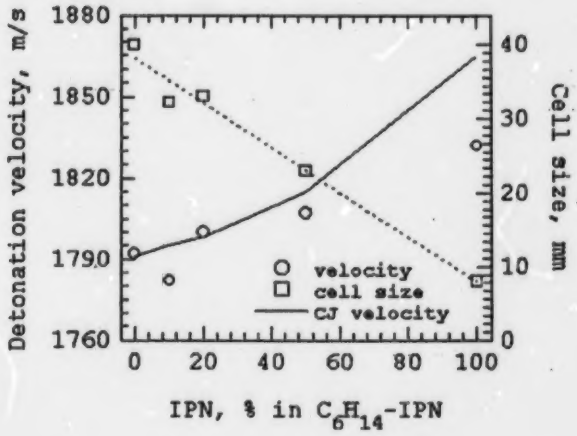
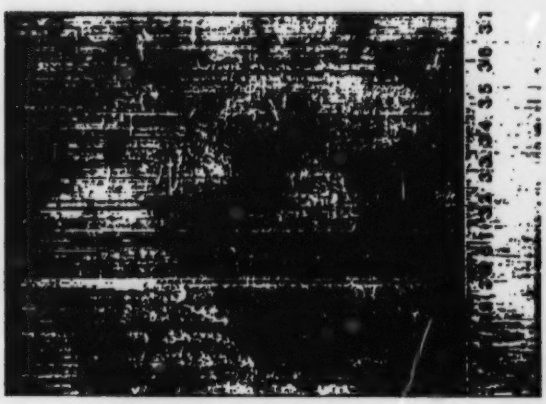
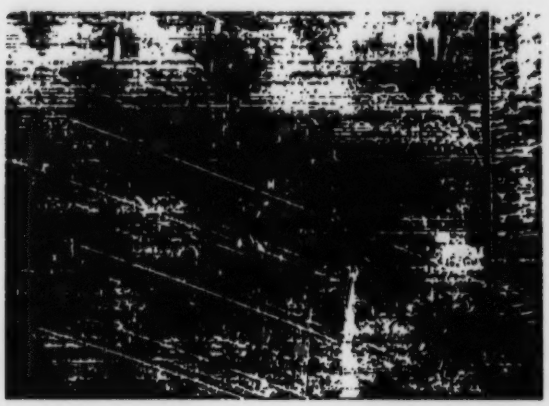


Figure 13. Detonation velocities and cell sizes for stoichiometric hexane-IPN-air mixtures at 1 atm and 388 K.

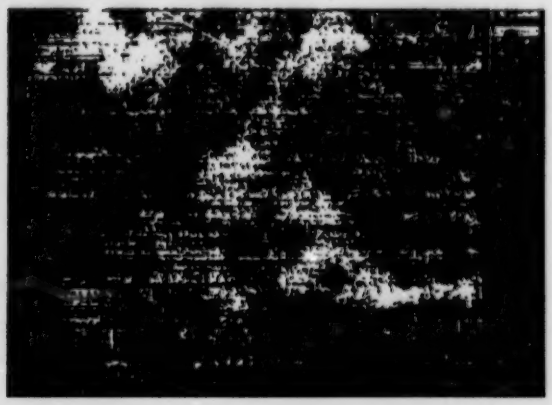


a. Hexane-air



b. (90% Hexane + 10% IPN)-air

c. (80% Hexane + 20% IPN)-air



d. (50% Hexane + 50% IPN)-air

e. IPN-air

Figure 14. Smoke foil record of cellular detonation for stoichiometric hexane-IPN-air at 1 atm and 388 K.

The smoke foil records are displayed in Fig. 14. These indicate that a multi-headed detonation with a strong transverse wave configuration propagates in various hexane-IPN-air mixtures. The measured detonation cell widths are summarized in Table 4 and Fig. 13. These were determined with a maximum deviation of about ±30 %. The detonation wave in IPN-air has a cell width of 8 mm, which is comparable to the detonation cell widths of the stoichiometric hydrogen-air (15 mm) and acetylene-air (6 mm) (Knystautas et al. 1984). The data from Knystautas et al. was measured at room temperature. Cicarelli et al. (1994) reported that the cell width for hydrogen-air was 8.2 mm at 300 K and 8.8 m at 500 K. Therefore, the dependence of the cell width on temperature over a range of 100 °C is weak. This was also indicated by Tieszen et al. (1991). Note that the mean cell size and its standard deviation for hexane-air were determined from two tests, 36 mm with a standard deviation of 7.6 mm for one test and 45 mm with a standard deviation of 8.5 mm for the other. The mean cell size (40 mm) of the two hexane-air tests is about 30 % smaller than that reported by Tieszen et al. (55 mm).

Among the hexane-IPN-air mixtures, the detonation cell width for IPN-air is the smallest, whereas that for the hexane-air is the largest. With an increase in the IPN concentration, the detonation cell size varies monotonically between that of the hydrocarbon fuel and IPN.

3.4 Discussions

The sensitization effect of some nitrates on shock ignition and detonation of hydrocarbons mainly originates in its oxygenated explosive nature. Nitrate compounds such as IPN can be considered monopropellants, which are generally known as low-sensitivity explosives. Liquid IPN has a theoretical CJ detonation velocity of 5860 m/s and a detonation pressure of 9.12 GPa, calculated using the Cheetah equilibrium code. Brochet (1970) measured the detonability of IPN and found that it varied with the confinement material, the charge diameter, and the initial conditions. At an initial temperature of 20 °C, the detonation reached a steady velocity of 5350 m/s in a steel tube 36 mm in inner diameter. Detonation failed when the charge diameter was reduced to 10 mm in a steel tube (see Fig. 15). In comparison, the critical diameter of nitromethane is 2.8 mm in a brass tube at the same initial temperature (Sherfield et al. 1999). The critical diameter of IPN in a steel tube observed by Brochet increased from 10 mm at 20 °C to 42 mm at 3 °C, which indicates the fact that the detonability of these liquid fuels is reduced when the initial temperature or the vapour pressure is decreased. For Pyrex and PVC (polyvinyl chloride) tubes, detonation was not observed for a charge diameter up to 42 mm at 57 °C.

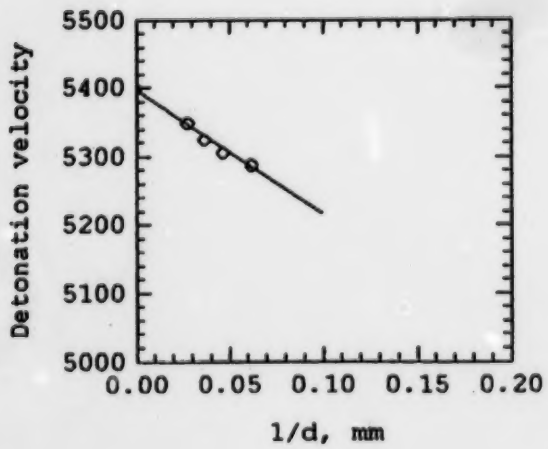


Figure 15. Detonation velocity versus charge diameter for propagation of detonation in liquid IPN at 20 °C confined by steel (Brochet 1970).

From the point of view of chemical kinetics, nitrates have a weaker bond, RO-NO_2, with a bond strength of 154 kJ/mole and a relative higher vapour pressure than most liquid fuels (Lu and Slagg 1972). Therefore, one can expect that IPN can decompose at lower temperatures. Consequently, the heat released and the radicals produced by the IPN reactions can be used to promote ignition and detonation of hydrocarbons. Whether the sensitizing effect on hydrocarbon detonation is mainly caused by the released heat or radicals of the nitrate is a fundamental problem requiring further detailed studies and eventually a quantitative description. However, the effect of these two factors can be qualitatively described by a global reaction extracted from the vapour-phase experiments.

The rate of a global vapour phase reaction of hydrocarbon-IPN in air:

$$\text{Hydrocarbon fuel} + (CH_3)_2CHNO_3 + \text{Air} \rightarrow \text{Products} \qquad (2)$$

can be described by the Arrhenius law determined by the exponential function of exp(-E/RT), where the parameter E is the effective activation energy per mole, the variable T is the temperature, and the parameter R is the universal gas constant. For shock induced detonations, an estimate of the shock temperature can be obtained from the one-dimensional ZND detonation model based on the frozen shock assumption:

$$\frac{T_{vN}}{T_0} = \frac{1}{M_{CJ}^2}\left[1+\frac{2\gamma}{\gamma+1}\left(M_{CJ}^2-1\right)\right]\left[1+\frac{\gamma-1}{\gamma+1}\left(M_{CJ}^2-1\right)\right] \qquad (3)$$

Hence, the shock temperature, T_{vN} (i.e., the von Neumann temperature), is determined by the detonation velocity squared, the specific heat ratio, and the initial sound speed or temperature. Because the detonation velocity squared is approximately proportional to the heat of reaction, Q, released in (2), the shock temperature is increased with the heat of reaction. Consequently, the exponential function in the Arrhenius law is determined by -E/T(Q), which states that a decrease in the activation energy or an increase in the heat of reaction will promote the reaction rate and therefore the detonability of the mixture.

From the above statement, it can be concluded that the extent of sensitization or desensitization of an additive at certain concentrations strongly depends on the difference of its activation energy and heat of reaction from those of a homogeneous fuel being sensitized. When the

activation energy of an additive is lower than that of a fuel and the heat of reaction of the additive is equal to or higher than that of the fuel, the combined effect of the activation energy and the heat of reaction will result in a monotonic increase of the fuel detonability with increases in the additive concentration. Our vapour phase detonation experiments have demonstrated this postulation. For shock ignition, the effective activation energy of IPN-air is almost half that of hexane-air (Table 3). On the other hand, the detonation velocity of IPN-air is comparable with hexane-air in the experiments. The CJ calculations indicate a slight increase in the heat of reaction by approximately 10 % for IPN over hexane. The combined effect of much lower activation energy and comparable energetics of IPN promotes the hydrocarbon vapour detonability, which manifests as monotonic decreases in the ignition delay and the detonation cell size with increases in the IPN concentration in fuel-IPN.

In the heterogeneous spray case, Borisov et al. (1983) also reported that the ignition delay varies monotonically between that for kerosene-air and IPN-air (see Fig. 16). A similar Arrhenius behavior was reported by Lu et al. (1972, 1974, 1977) for heptane and kerosene in air sensitized by propyl nitrate (NPN). Note that like the hexane used in this report, heptane has a higher vapour pressure than NPN, whereas kerosene possesses a lower vapour pressure (Tables 1 and 2). Hence, these experiments show that the influence of the vapour pressure becomes less significant than the heat and kinetics effects induced by the nitrate. Although further detailed studies are necessary, these experimental evidences indicate that the detonation sensitization of hydrocarbon spray by liquid IPN or NPN might also largely depend on the combined effects of the activation energy and the energetics of the nitrate used.

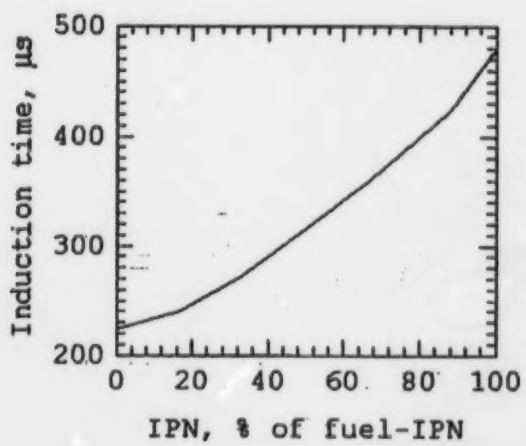


Figure 16. Induction time for kerosene spray in air with IPN additive (Borisov et al. 1983).

If both the activation energy and the heat of reaction of an additive are lower than those of a liquid fuel, there can exist a critical additive concentration between 0 and 100 %. Below this critical concentration, the sensitizing effect caused by the lower activation energy overwhelms the desensitizing effect of the lower heat of reaction. Therefore, the additive effectively promotes the ignition of hydrocarbon fuels at low concentrations of the additive. Above the critical concentration, the lower heat of reaction becomes the main factor, thus resulting in a desensitizing effect on the hydrocarbon fuels at high concentrations of the additive. Good experimental evidence of this competition between the activation energy and the energetics can be found in the work by Borisov et al. (1983) for dodecatriene mixed with 1,4-butandiol dinitrates, and Lee et al. (1999) for nitromethane with amine additives.

4. Conclusions

For a spray consisting of hydrocarbon liquid droplets and air, the literature shows that the shock ignition and detonability can be promoted by adding nitrates. This sensitizing effect has been considered the result of reaction kinetics promotion via the formation of radicals in the literature. In view of the fact that these nitrates contain oxygen in their molecular structure and can be considered a low-sensitivity condensed explosive, the sensitization effect of the nitrates could be interpreted alternatively as the micro-scale decomposition or explosion of nitrate particles which produce heat and radicals. Although the fundamental question, (i.e., whether the sensitizing effect is caused mainly by radical kinetics or by the micro-scale explosion of nitrate particles for a spray) can only be solved under heterogeneous conditions, vapour phase studies at elevated temperature provide a lower limit approach for insight into the relevant mechanism involved.

Isopropyl nitrate (IPN) was chosen due to its low-sensitivity explosive nature. The shock ignition and detonation experiments were performed in stoichiometric hexane-IPN-air vapour mixtures with an IPN concentration ranging from 0 to 100 mole % in the total fuel of hexane-IPN. The results demonstrate that the ignition delay and the detonation cell size are the smallest for IPN-air and the largest for hexane-air. With an increase in the IPN concentration, the ignition delay and the detonation cell size fall between those of hexane and IPN. This monotonic behavior of the sensitizing effect has been interpreted as the combined effect of the lower activation energy and the comparable heat of reaction possessed by IPN. From the Arrhenius law, the extent of sensitization or desensitization of an additive at certain concentrations strongly depends on the difference between the activation energy and the heat of reaction of an additive and those of the homogeneous fuel to be sensitized. Because IPN has a lower activation energy and a comparable heat of reaction, an increase in IPN concentration

elevates the reaction rate in a monotonic fashion and results in a reduction in the ignition delay and the detonation cell size of the hydrocarbon fuel.

The sensitizing effect of IPN was also investigated in the slow combustion mode by measuring the lean flammability limits and flame velocities of methane, propane and hexane in air. The results also confirm the monotonic behavior and show that the lean flammability limit and the flame velocity fell between those of the fuel and its additive.

Acknowledgements

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References

Bar-Or R, Sichel M, Nicholls, JA (1981) The propagation of cylindrical detonations in monodisperse sprays. 18th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, pp 1599-1606

Benedick WB, Tieszen R, Knystautas R, Lee JHS (1991) Detonation of unconfined large-scale fuel spray-air clouds. In: Kuhl AL, Leyer J-C, Borisov AA, Sirigano WA (eds) Dynamics of detonations and explosions: detonations. Progress in Astronautics and Aeronautics 133, AIAA Inc., New York, pp 297-310

Borisov AA, Gelfand BE, Gubin SA, Kogarko, SM, Podgrebenkov AL (1970) The reaction zone of two-phase detonations. Astronautica Acta 15:411

Borisov AA, Gelfand BE, Timofeev EI, Tsyganov SA (1983) Self-ignition of atomized liquid fuel in gaseous medium. In: Bowen JR, Manson N, Oppenheim AK, Soloukhin RI (eds) Shock waves, explosions, and detonations. Progress in Astronautics and Aeronautics 87, AIAA, Inc., New York, pp 240-251

Borisov AA, Gelfand, BE, Dragalova, EV (1983) Khim Fiz 2:838

Brochet C (1970) Monopropellant detonation: isopropyl nitrate. Astronautic Acta 15:419

Bull DC, Elsworth JE, McLeod MA (1981) Detonation of unconfined fuel aerosols. In: Bowen JR Manson N, Oppenheim AK, Soloukhin RI (eds) Gasdynamics of detonations and explosions. Progress in Astronautics and Aeronautics 75, AIAA Inc., New York, pp 48-60

Ciccarelli G, Ginsberg T, Boccio J, Economos C, Sato K, Kinoshita M (1994) Detonation cell size measurements and predictions in hydrogen-air-steam mixtures at elevated temperatures. Combustion and Flame, 99:212

Combustion Dynamics Ltd. (CDL) (1996) Theoretical and User Manuel for Super State Code

Dabora EK, Ragland KW, Nicholls JA (1969) Drop size effects in spray detonations. In: 12th Symposium (International) on Combustion, The combustion Institute, Pittsburgh, Pennsylvania, pp 19-26

Dabora EK, Ragland KW, Nicholls JA (1968) The observed structure of spray detonations. Phys. Fluids 11:2377

Dabora EK, Fox GE (1972) The breakup of liquid droplet columns by shock waves. Astronautica Acta 17:669

Dabora EK. (1980) Effect of additives on the lean detonation limit of kerosene in air. Final Report, the U. S. Army Research Office under Grant DAAG 29-78-G0074, UCONN Report 0507-129-F, University of Connecticut, Storrs, Connecticut 06268

Engelke R (1980) Effect of a chemical inhomogeneity on steady state detonation velocity. Phys. Fluids 23:875

Engelke R (1986) Earl WL, McMichael Rohling C (1986) Microscopic evidence that the nitromethane aci ion is a rate controlling species in the detonation of liquid nitromethane. J. Chem. Phys. 84:142

Knystautas R, Guirao C, Lee JH, Sulmistras A (1984) Measurements of cell size in hydrocarbon-air mixtures and predictions of critical tube diameter, critical initiation energy, and detonability limits. In: Bowen JR, Manson M, Oppenheim AK, Soloukin RI (eds) Dynamics of shock waves, explosions, and detonations. Progress in Astronautics and Aetonautics 94, AIAA Inc., New York, pp 23-37

Lee JJ, Jiang J, Choong KH, Lee JHS (1999) Effect of diethylenetriamine and triethylamine sensitization on the critical diameter of nitromethane. 11th APS group meeting: Shock Compression of Condensed Materials, Snowbird, Utah

Lin ZC, Nicholis JA, Tang MJ, Kaufmann CW, Sichel M (1984) Vapor pressure and sensitization effects in detonation of a decane spray. 20th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, pp 1709-1716

Lu PL, Slagg N (1972) Chemical aspects in the shock initiation of fuel droplets. Astronautica Acta 17:693

Lu PL, Slagg N (1974) Chemical aspects in shock initiation of fuel drops," Acta Astronautics 1:1219

Lu PL, Slagg N, Fishburn BD (1977) Relation of chemical and physical processes in two phase detonations. 6th International Colloquium on Gas Dynamics of Explosions and Reactive Systems, Stockholm, Sweden

Murray SB, Gerrard KB (1990) Field studies of fuel-air explosive line charges: a summary report for the 65-mm charge. DRES Report No. 534, Defence Research Establishment Suffield.

Presles HN, Desbordes D, Guirard M, Guerrand C (1996) Gaseous nitromethane and nitromethane-oxygen mixtures: a new detonation structure. Shock Waves 6:111

Sherfield SA, Davis LL, Engelke R (1999) Detonation properties of nitromethane, deuterated nitromethane and bromonitromethene. 11th APS Topical Group Meeting on Shock Compression of Condensed Matter, Snowbird, Utah

Sichel M (1982) The detonation of sprays: recent results. In: Lee JHS, Guirao, CM (eds) Fuel-air explosions. University of Waterloo Press, pp 265-302

Tang MJ, Nicholls JA, Lin ZC, Sichel M, Kauffman CW (1986) Direct initiation of detonation in a decane spray. In: Bowen JR, Leyer J-C, Soloukin RI (eds) Dynamics of explosions. Progress in Astronautics and Aetonautics 106, AIAA, Inc., New York, pp 474-489

Tieszen SR, Stamps DW, Westbrook CK, Pitz WJ (1991) Gaseous hydrocarbon – air detonations. Combustion and Flame, 84:376

Wagner et al. (1972) Verhalten der Brennstoffe und Verbrennungsabgase bei der Verbrennung. In: Borchers H, Hausen H, Hellwege K-H, Schaefer KL, Schmidt E (eds) Landolt-Boernstein Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik, Band VI: Technik, Teil 4: Waemetechnik, Springer-Verlag, Berlin, p. 333-393

Walker FE (1979) Initiation and detonation studies in sensitized nitromethane," Acta Astronautica 6:807

Zaslonko IS, Kochergina TI, Mukoseev Yu-K, Petrov Yu-P, Smirnov VN, Tereza AM (1985) Thermal decomposition of nitrates – promoters of hydrocarbon ignition. Soviet Journal of Chemical Physics, 2:1763

Zaslonko IS, Smirnov VN, Tereza AM, Tsyganov SA (1988) Kinetics of energy liberation during thermal decomposition Fizika Goreniya i Vzryva, 24:137

Zhang F, Thibault PA, Murray SB (1998) Transition from deflagration to detonation in an end multiphase slug. Combustion and Flame 114:13

Appendix 2

Experimental Data From the 8-cm Shock Tube

Test ID	Driver P [atm]	Driver Gas	Test Mix	Test P [atm]	$\Delta\tau_{expt}$ [ms]	Incident Shock Speed [m/s]	Calculated Temperature Behind Refl. Shock [K]
102698a	10	N2	Equimolar	0.25	1.77	670	741
102798a	10	N2	Equimolar	0.25	1.79	674	747
110598a	11	N2	Equimolar	0.25	0.90	708	796
110598b	12	N2	Equimolar	0.25	0.42	770	889
110998a	11	N2	Equimolar	0.25	0.41	824	975
103098	5	N2	Pure IPN	0.25	1.324	568.6	602
110298	5	N2	Pure IPN	0.25	1.51	563	595
110398a	7	N2	Pure IPN	0.25	0.70	607	654
110698	6	N2	Pure IPN	0.25	0.70	607	653
110698a	7	N2	Pure IPN	0.25	0.68	625	678
111098	6	N2	Pure IPN	0.25	0.95	604	650
110498	10	He	Pure Hexane	0.25	0.74	962	1209
110498a	11	He	Pure Hexane	0.25	0.55	1000	1278
110998	9	He	Pure Hexane	0.25	1.25	921	1136
111098a	11	He	Pure Hexane	0.25	0.64	988	1255
111098b	9	He	Pure Hexane	0.25	1.00	926	1146
102898	10	N2	0.2 IPN + 0.8 Hexane	0.25	4.73	662	730
102898a	10	N2	0.2 IPN + 0.8 Hexane	0.25	5.00	670	741

Table 1 A.: Summary of ignition delay results from the 8-cm tube.

The following are traces from the pressure transducer at the end wall, recorded in the ignition delay tests of Table 1 A.

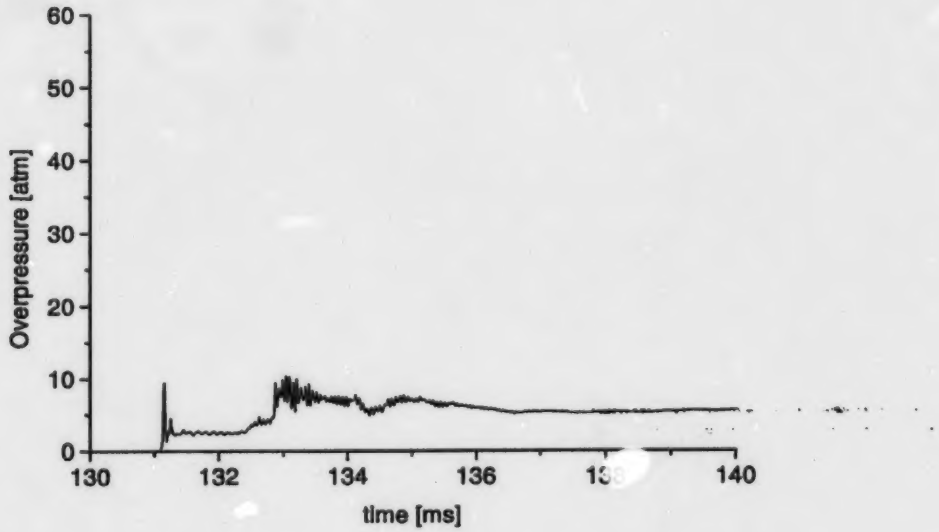

Figure 1A: Shot 102698a stoichiometric 50% IPN 50 % Hexane and Air.
10 atm nitrogen driver.

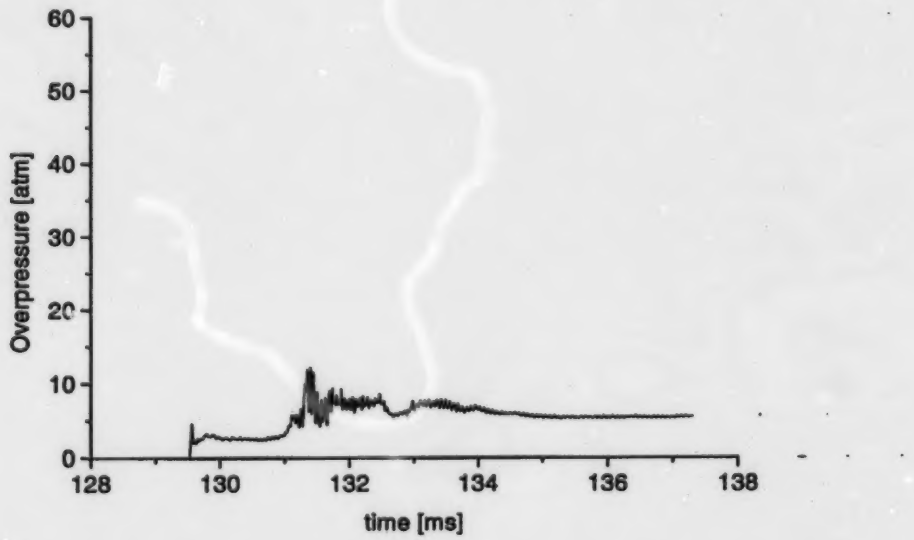

Figure 2A: Shot 102798a, stoichiometric 50% IPN 50% Hexane and Air.
10 atm nitrogen driver.

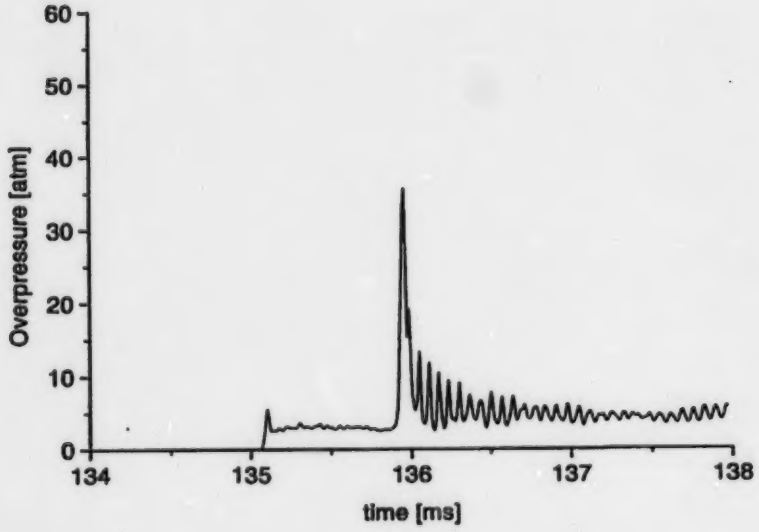

Figure 3A: Shot 110598a. Stoichiometric 50 % IPN + 50 % Hexane and Air. 11 atm nitrogen driver.

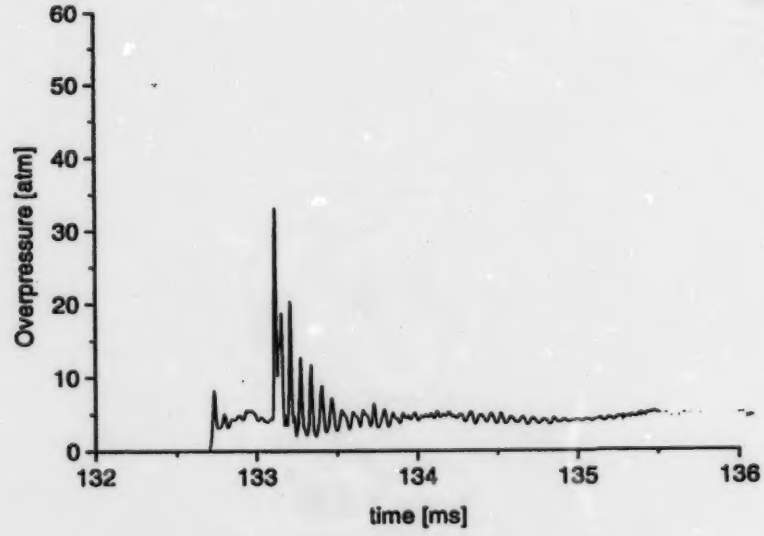

Figure 4A: Shot 110598b. Stoichiometric 50 % IPN + 50 % Hexane and Air. 12 atm nitrogen driver.

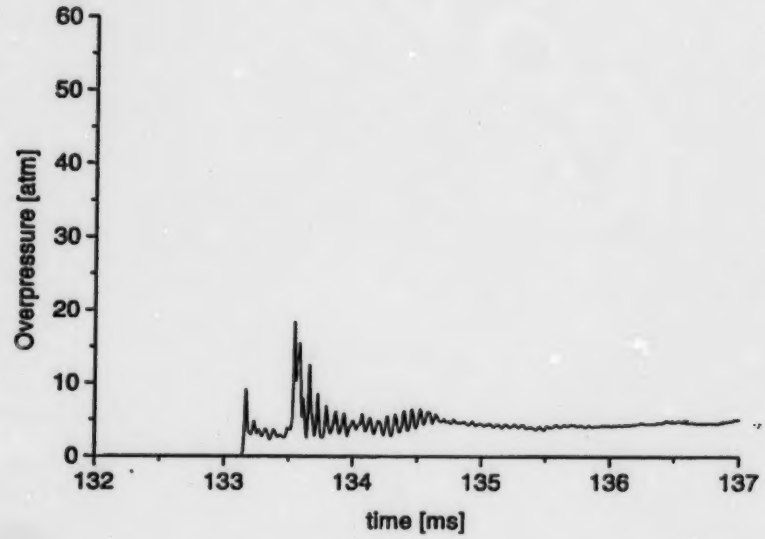

Figure 5A: Shot 110998a. Stoichiometric 50 % IPN + 50 % Hexane and Air. 11 atm nitrogen driver.

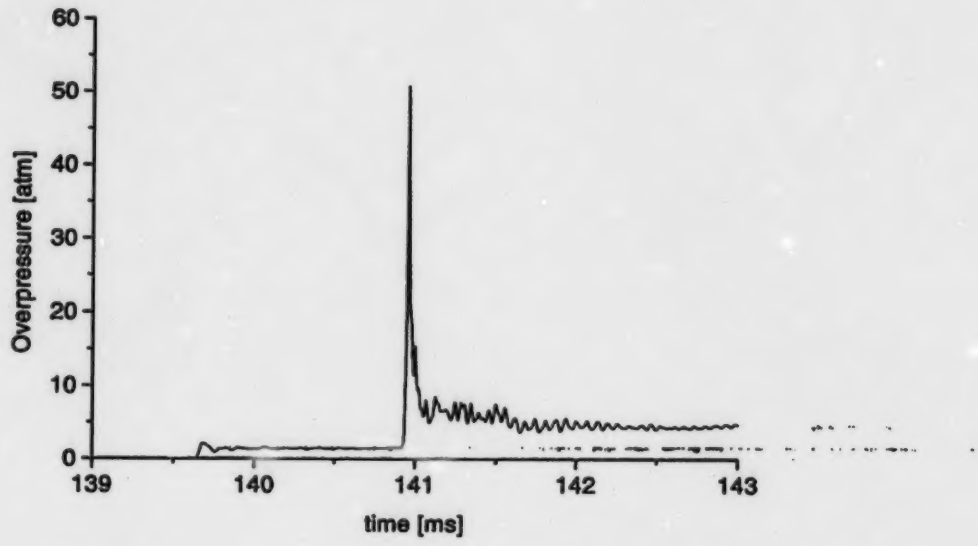

Figure 6A: Shot 103098. Stoichiometric IPN and Air. 5 atm nitrogen driver.

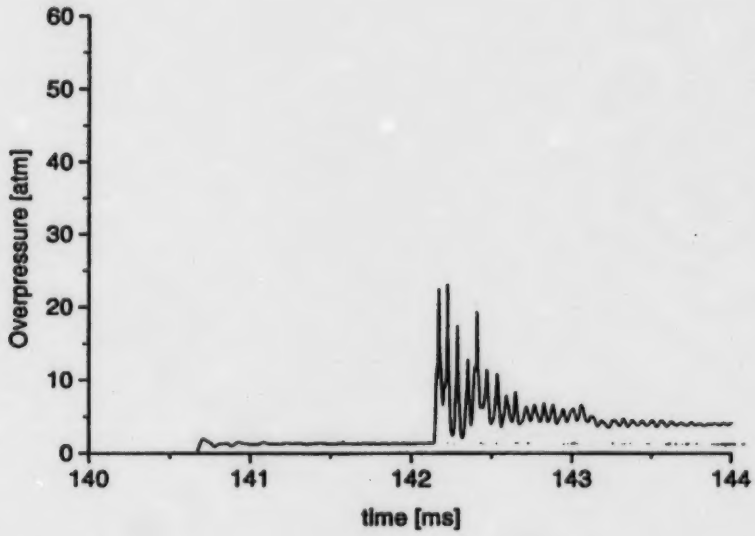

Figure 7A: Shot 110298. Stoichiometric IPN and Air. 5 atm nitrogen driver.

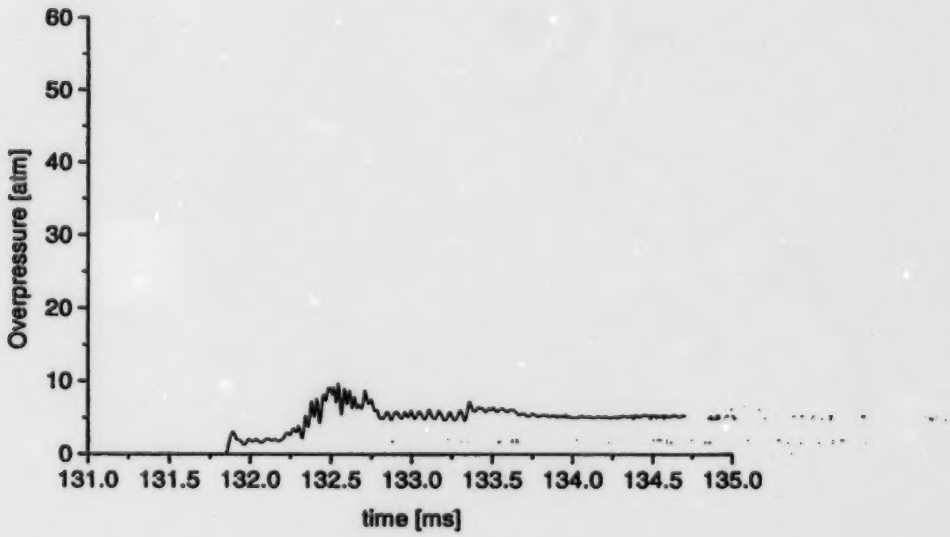

Figure 8A: Shot 110398a. Stoichiometric IPN and Air. 7 atm nitrogen driver.

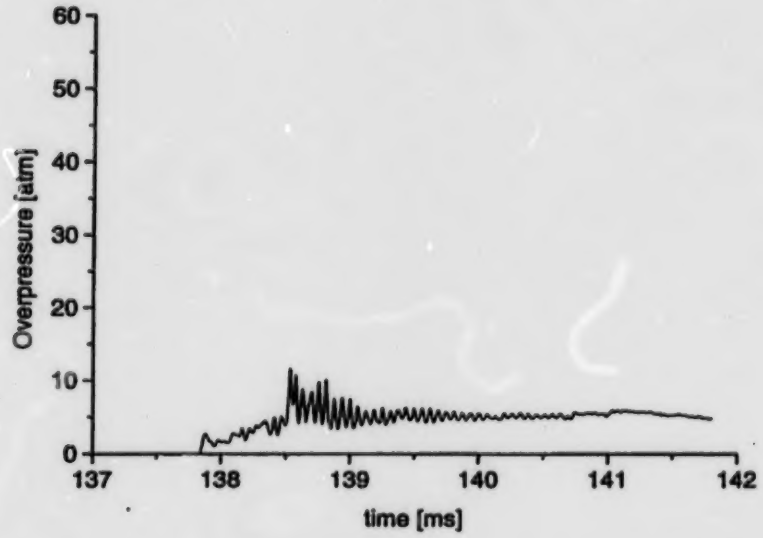

Figure 9A: Shot 110698. Stoichiometric IPN and Air. 6 atm nitrogen driver.

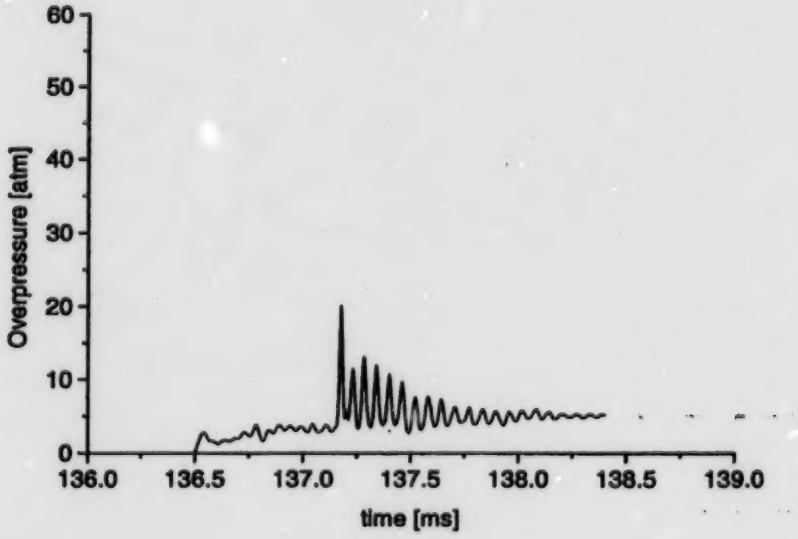

Figure 10A: Shot 110698a. Stoichiometric IPN and Air. 7 atm nitrogen driver.

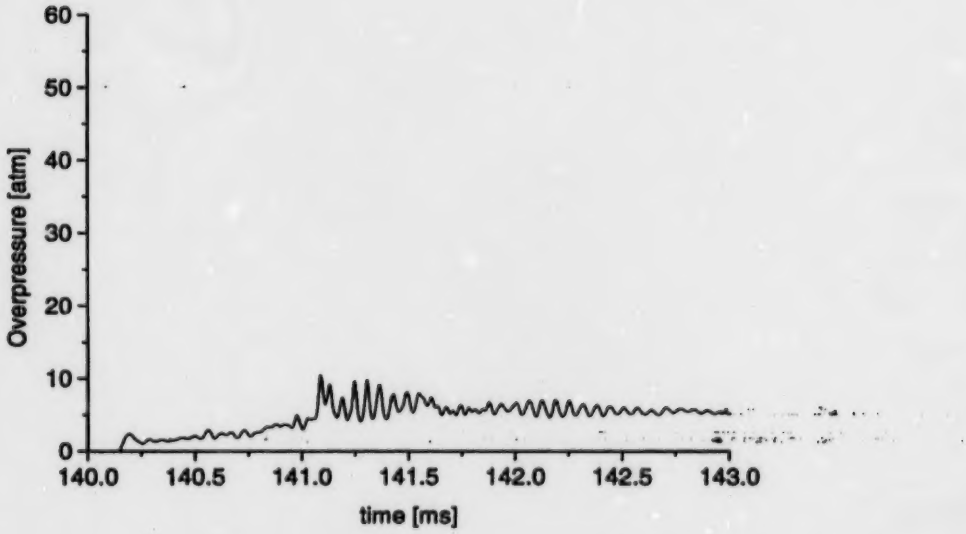

Figure 11A: Shot 111098. Stoichiometric IPN and Air. 6 atm nitrogen driver.

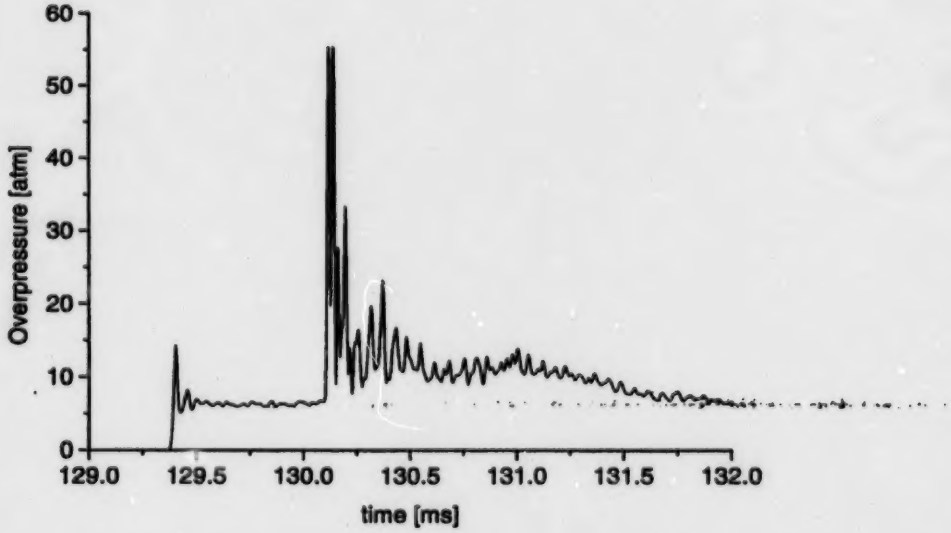

Figure 12A: Shot 110498. Stoichiometric Hexane and Air. 10 atm helium driver.

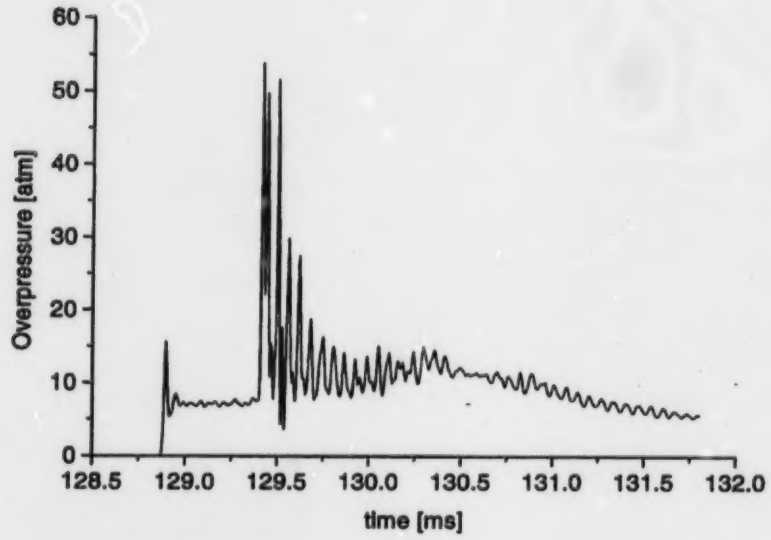

Figure 13A: Shot 110498a. Stoichiometric Hexane and Air. 11 atm helium driver.

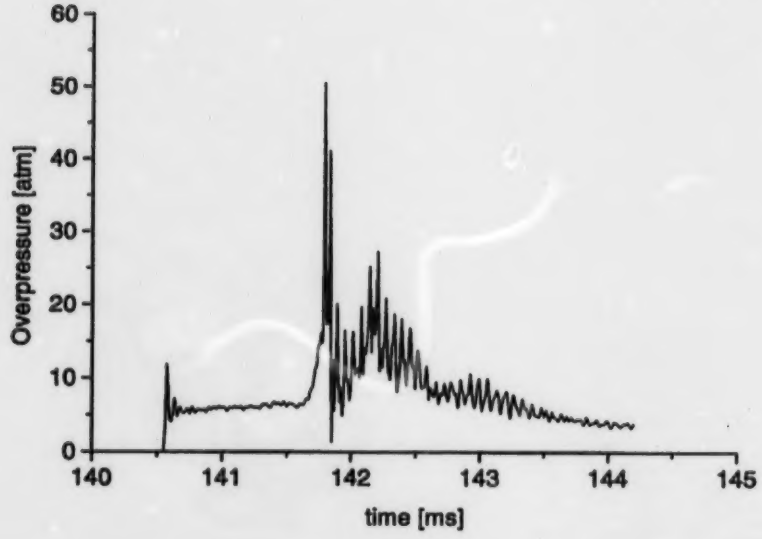

Figure 14A: Shot 110998. Stoichiometric Hexane and Air. 9 atm helium driver.

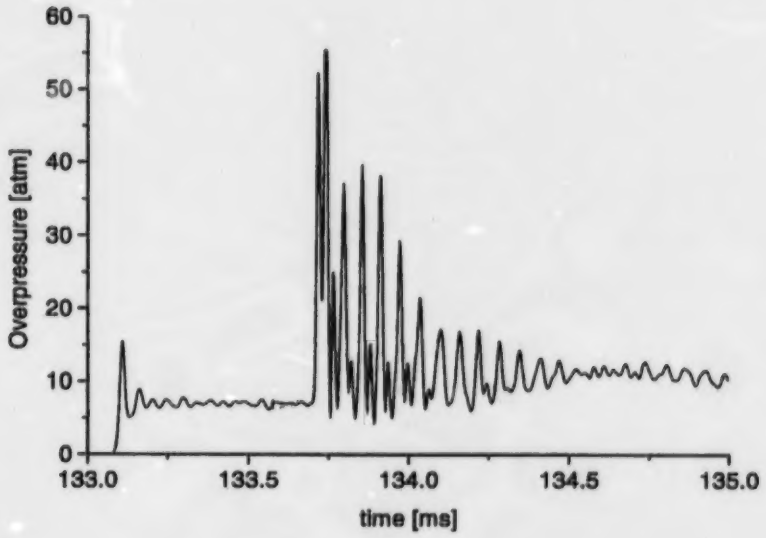

Figure 15A: Shot 111098a. Stoichiometric Hexane and Air. 11 atm helium driver.

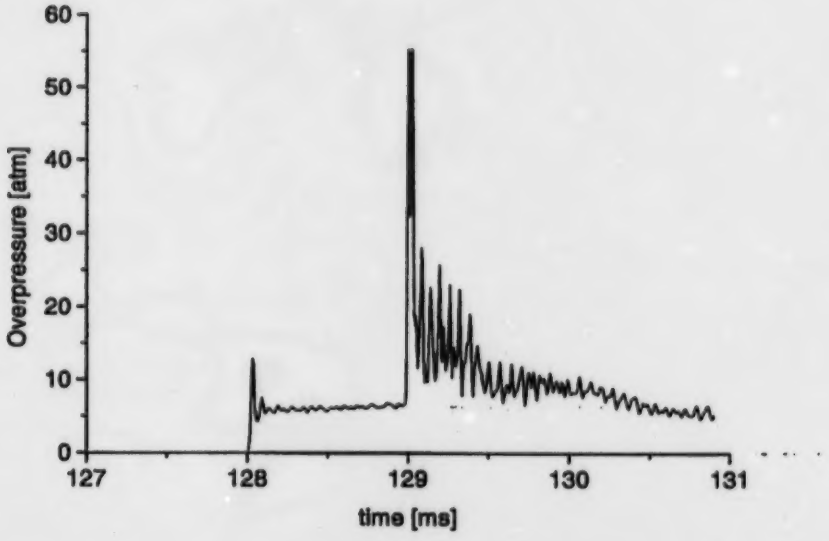

Figure 16A: Shot 111098b. Stoichiometric hexane and air. 9 atm helium driver.

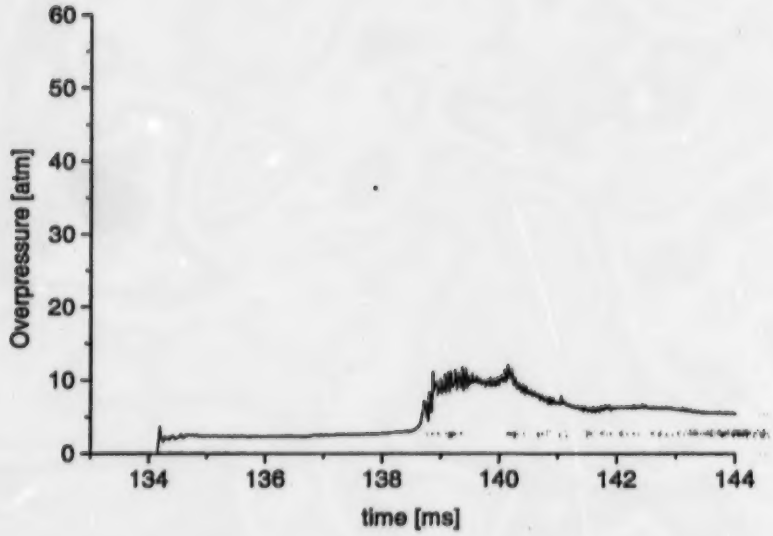

Figure 17A: Shot 102898. Stoichiometric, 20% IPN + 80% Hexane, and Air. 10 atm nitrogen driver.

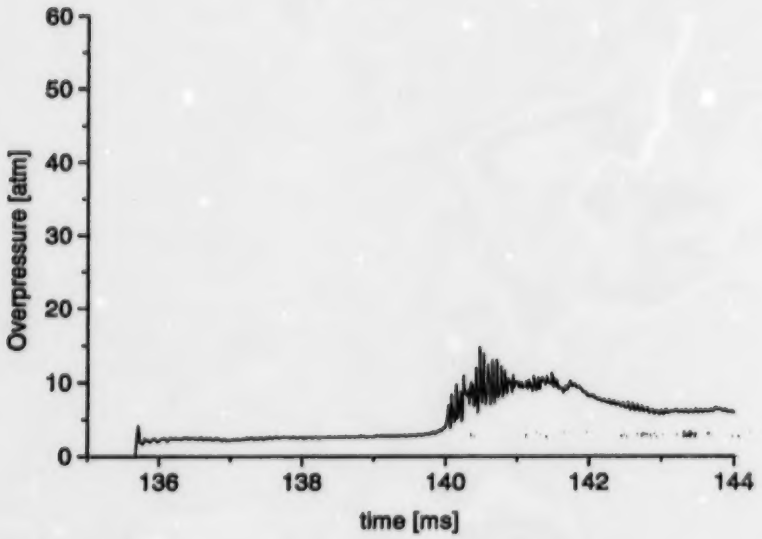

Figure 18A. Shot 102898a Stoichiometric 20% IPN + 80% Hexane, and Air. 10 atm nitrogen driver.

Appendix 3

Experimental Data from the 30-cm Detonation Tube

Shot ID	24.6 m (driver)	23 m	5 m	4 m	3 m	2 m	1 m
D99125a	P	P	P	P	P	X	X
D99133a	P	X	P	P	P	X	P
D99138a	P	X	I	P+I	P	X	I
D99140a	P	X	I	P+I	P	I	I
D99146a	P	X	I	I	P	I	I
D99148	P	X	I	I	I	I	I

Table 1B: Gage deployment in shots using the 30-cm tube. I denotes an ionization gage, P denotes a pressure gage, and X denotes none. More than one gage at the same position indicates that opposing ports were used. All distances are measured from the relief diaphragm backwards to the relevant port. Note that the soot foil lies just before the relief diaphragm, and the last 5 metres are within the same test section as the soot foil. Note that some transducer traces are missing in the plots that follow, due to instrument failure.

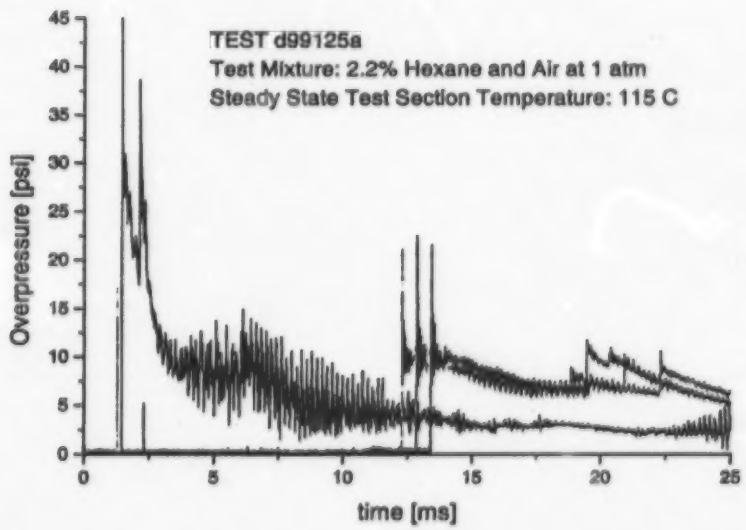

Figure 1B: Shot D99125a, 2.2 % Hexane and Air mixture. Pressure traces in the driver and soot foil sections, at 24.6 m, 5 m, 4 m and 3 m from the relief diaphragm.

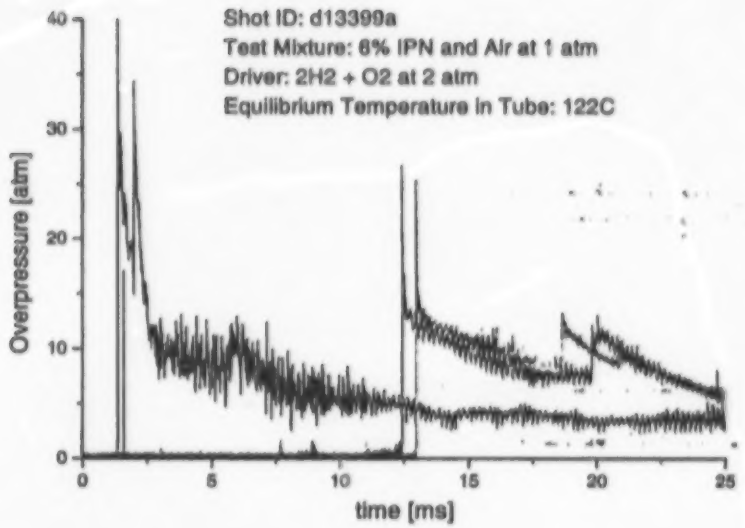

Figure 2B: Shot D99133A, 6% IPN and Air mixture. Pressure traces in the driver and soot foil sections, at 24.6 m, 4 m and 3 m from the relief diaphragm.

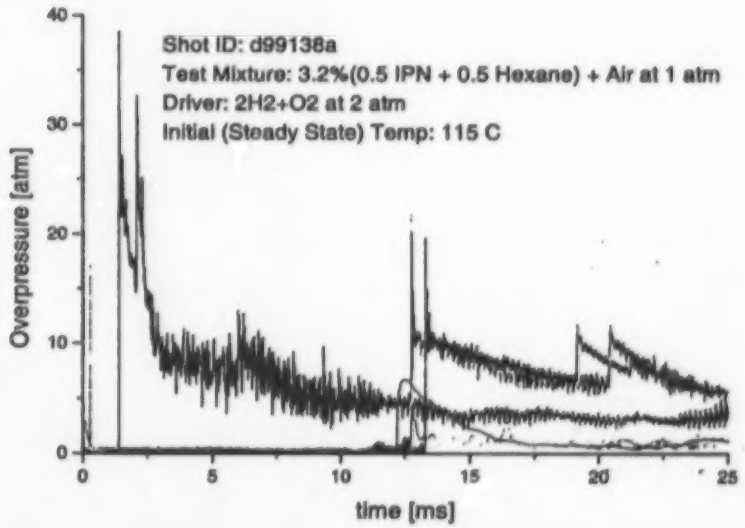

Figure 3B: Shot D99138a, 3.2% (0.5 IPN + 0.5 Hexane) and Air. Pressure and ionization gage traces in driver and soot foil sections. Pressure gages are at 24.6 m, 4 m and 3 m from the relief diaphragm. Ionization gages are at 5 m and 4 m from the relief diaphragm.

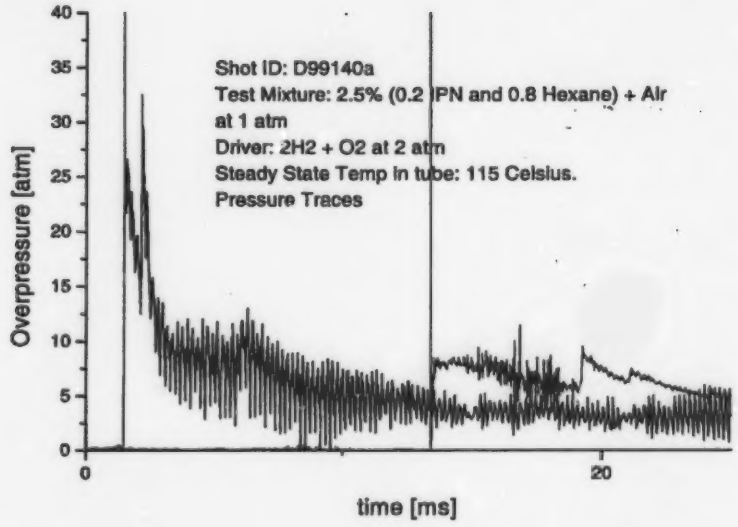

Figure 4B: Shot D99140a of 2.5% (0.2 IPN and 0.8 Hexane) and Air. Pressure traces in driver section and soot foil section at 24.6 m and 3 m from the relief diaphragm.

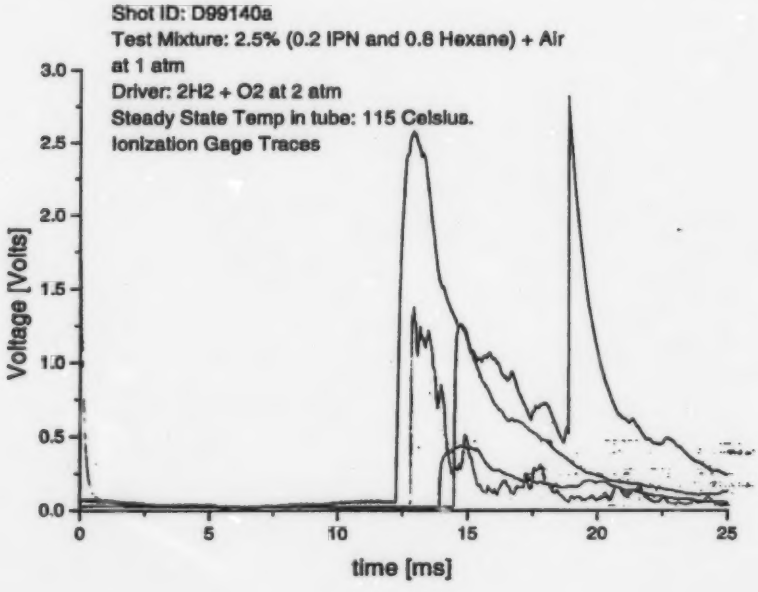

Figure 5B: Shot D99140a of 2.5% (0.2 IPN and 0.8 Hexane) and Air. Ionization gage traces in the soot foil section, at 5 m, 4 m, 2 m and 1 m from relief diaphragm.

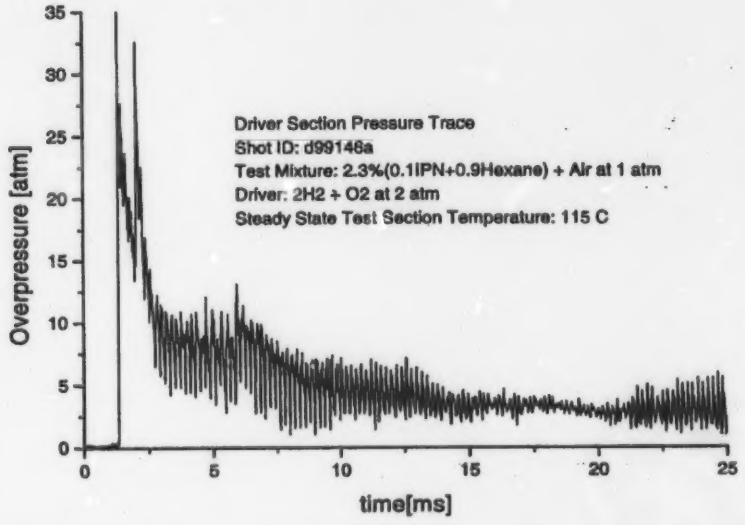
Driver Section Pressure Trace
Shot ID: d99146a
Test Mixture: 2.3%(0.1IPN+0.9Hexane) + Air at 1 atm
Driver: 2H2 + O2 at 2 atm
Steady State Test Section Temperature: 115 C
Overpressure [atm]
time[ms]

Figure 6B: Shot D99146a of 2.3%(0.1 IPN and 0.9 Hexane) and Air. Pressure trace in driver.

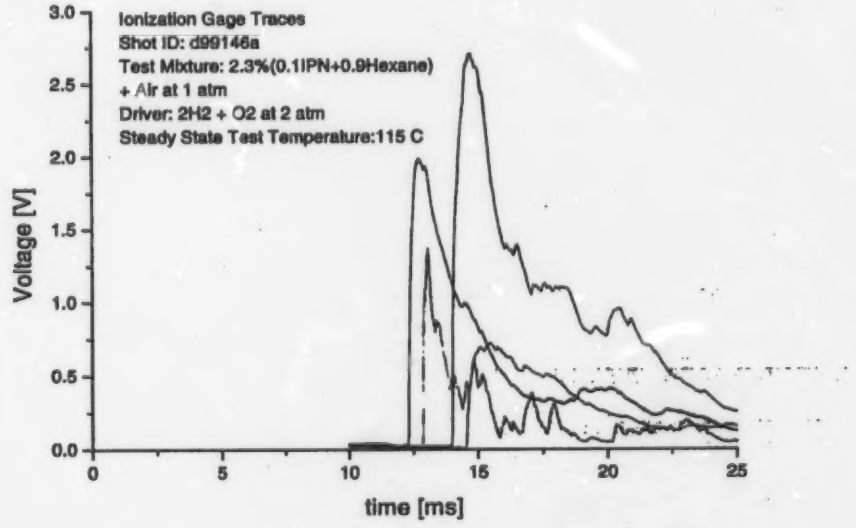

Figure 7B: Shot D99146a of 2.3%(0.1 IPN and 0.9 Hexane) and Air. Ionization gage traces in soot foil section, at 5m, 4m, 2 m and 1 m from relief diaphragm.

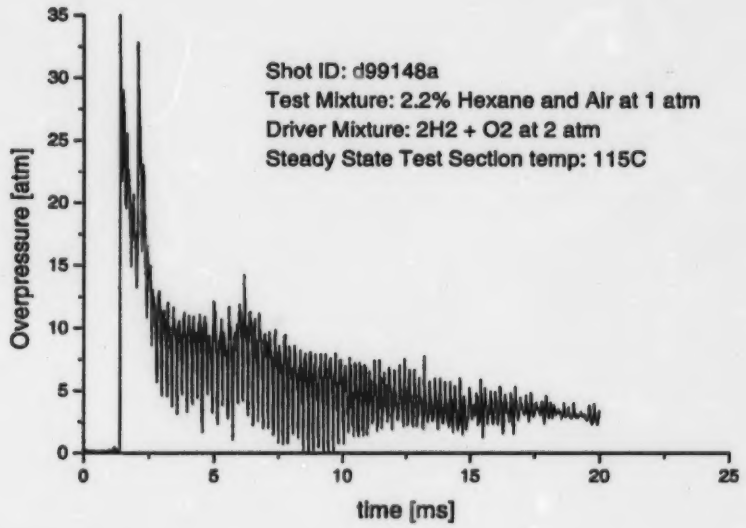

Figure 8B: Shot D99148a of 2.2% Hexane and Air. Pressure transducer in driver section.

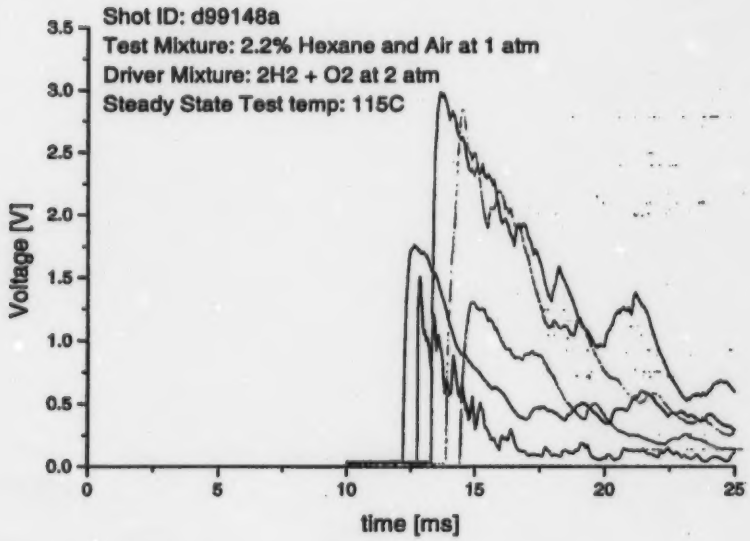

Figure 9B: Shot D99148a of 2.2% Hexane and Air. Ionization gage traces in soot foil section, at 5 m, 4 m, 3 m, 2 m and 1 m from relief diaphragm.

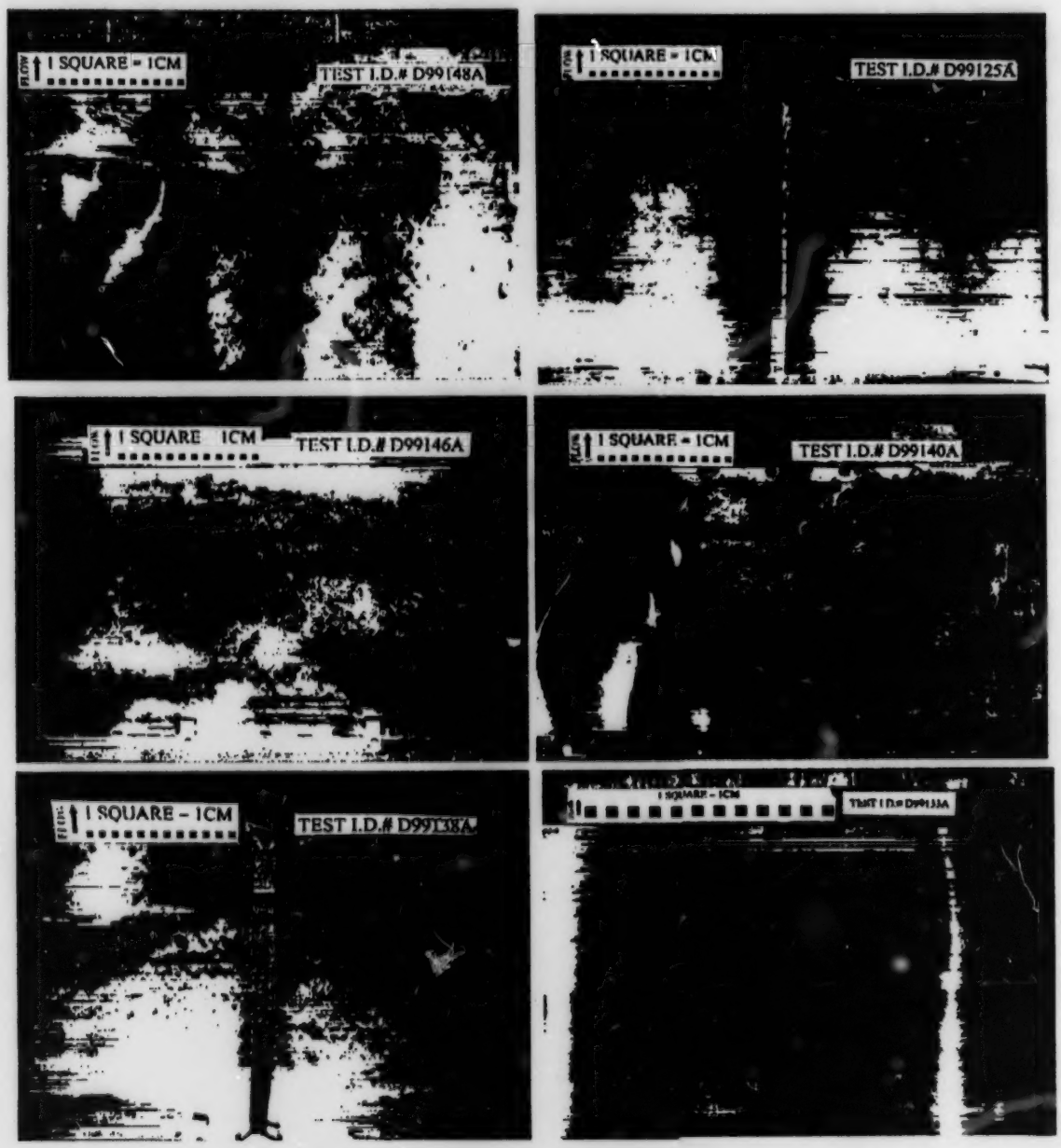

Figure 10B: Photographs of soot foils of the detonation tests in the 30-cm tube. For the mixtures corresponding to the Shot ID numbers, refer to Figures 1B-9B.